LIGNIN-DERIVED ORGANIC MATTER IN GEORGIA COASTAL WATERS

Mary Ann Moran, Lawrence R. Pomeroy, Edward S. Sheppard, Larry P. Atkinson, and Robert E. Hodson

AUTHORS: Mary Ann Moran, Edward S. Sheppard, and Robert E. Hodson, Department of Microbiology and Institute of Ecology, The University of Georgia, Athens, GA 30602; Lawrence R. Pomeroy, Department of Zoology and Institute of Ecology, The University of Georgia, Athens, GA 30602; Larry P. Atkinson, Oceanography Department, Old Dominion University, Norfolk, VA 23529.
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INTRODUCTION

The importance of riverine- and saltmarsh-derived organic matter to the food web of Georgia coastal waters has been a focus of ecological research over the past thirty years. Studies based on energy budgets, carbon flux measurements, and stable isotope ratios have generally implicated marsh detritus as an important, although not always dominant, source of organic matter within the marshes and adjacent estuaries (Teal 1962, Odum and de la Cruz 1967, Haines 1977, Peterson and Howarth 1987). However, data on the contribution of exported marsh and riverine organic matter to productivity further offshore, in continental shelf waters off the coast of Georgia, remains equivocal (Chalmers et al. 1985, Hopkinson 1985).

Dissolved lignin-derived compounds provide molecular-level markers by which to determine the presence of terrestrially-derived organic matter in marine ecosystems. Lignin is found only in vascular plants and has no known oceanic sources. Thus its presence in seawater serves as unequivocal evidence of input of marsh or riverine organic matter, and indeed such lignin-derived material has been found in open ocean water a great distance from its probable point of origin (Meyers-Schulte and Hedges 1986). In this study, we present data on concentrations and distribution of lignin phenols in seawater samples collected during October and November 1987 on the continental shelf of the southeastern U.S., between Cape Hattaras and Cape Canaveral.

METHODS

The continental shelf of the southeastern U.S. varies in width, extending up to 200 km off the coast of Georgia. Within our study area, the coastline is highly indented with inlets connecting rivers and coastal marshes to the Atlantic Ocean. The Savannah, Altamaha, Ogeechee, Satilla, and St. Johns Rivers account for the bulk of freshwater discharge (Blanton 1980). Extensive salt marshes, located behind the barrier islands of Georgia, are in contact with coastal water during the twice-daily flooding.

Seawater samples were collected from surface waters (1-2 m depth) on the continental shelf off the coasts of Georgia and north Florida during an October 23 to November 6, 1987 cruise aboard the R.V. Columbus Iselin (Figure 1). The 40-liter water samples were filtered through glass fiber filters and acidified to pH 2. Humic substances were isolated by pumping the water through a column containing Amberlite XAD-8 resin. At low pH, humic substances are in protonated form and adhere to the resin. Humics were eluted from the resin with 0.1 N NaOH and the eluant was pumped through an AG-MP50 cation exchange resin (Aiken 1985). Humic materials were concentrated by rotary evaporation, freeze-dried, and stored frozen until lignin analysis.

For lignin phenol analysis, humic substances were reacted with alkaline cupric oxide for 3 h at 170°C to produce a suite of lignin phenols. Phenols were extracted from the oxidation mixture with ether and converted to trimethylsilyl derivatives. Separation and quantification of phenol derivatives was carried out using HP 5890 gas chromatographs equipped with Supelco SE-30 and J & W DB-1701 polysiloxane columns (Hedges and Ertel 1982, Hedges et al. 1988) The concentrations of three vanillyl phenols (vanillic acid, vanillin, and acetovanillon) were summed and expressed in units of $\mu g\ L^{-1}$.

Additional samples were collected from water bodies serving as sources of lignin phenols to Georgia coastal water, including a salt marsh creek (Duplin River, Sapelo Island), the Altamaha, Savannah, and Hampton Rivers, and Ossabaw Sound. All water samples were filtered and acidified, and humic substances were isolated and analyzed for lignin phenol concentrations as described above.

RESULTS AND DISCUSSION

During degradation of submerged detrital vascular plant material by marine bacteria, soluble compounds are released through physical leaching processes and the activities of bacterial exoenzymes (Moran and Hodson 1989). While some fraction of these degradation products is utilized immediately by bacteria associated with the degrading plant detritus, other fractions of the solubilized material become components of the dissolved organic carbon (DOC) pool in marine environments. The fate of this vascular plant-derived DOC may be eventual incorporation into marine food webs following bacterial utilization, or long-term storage in the DOC pool as degradation-resistant humic substances (Moran and Hodson 1990).

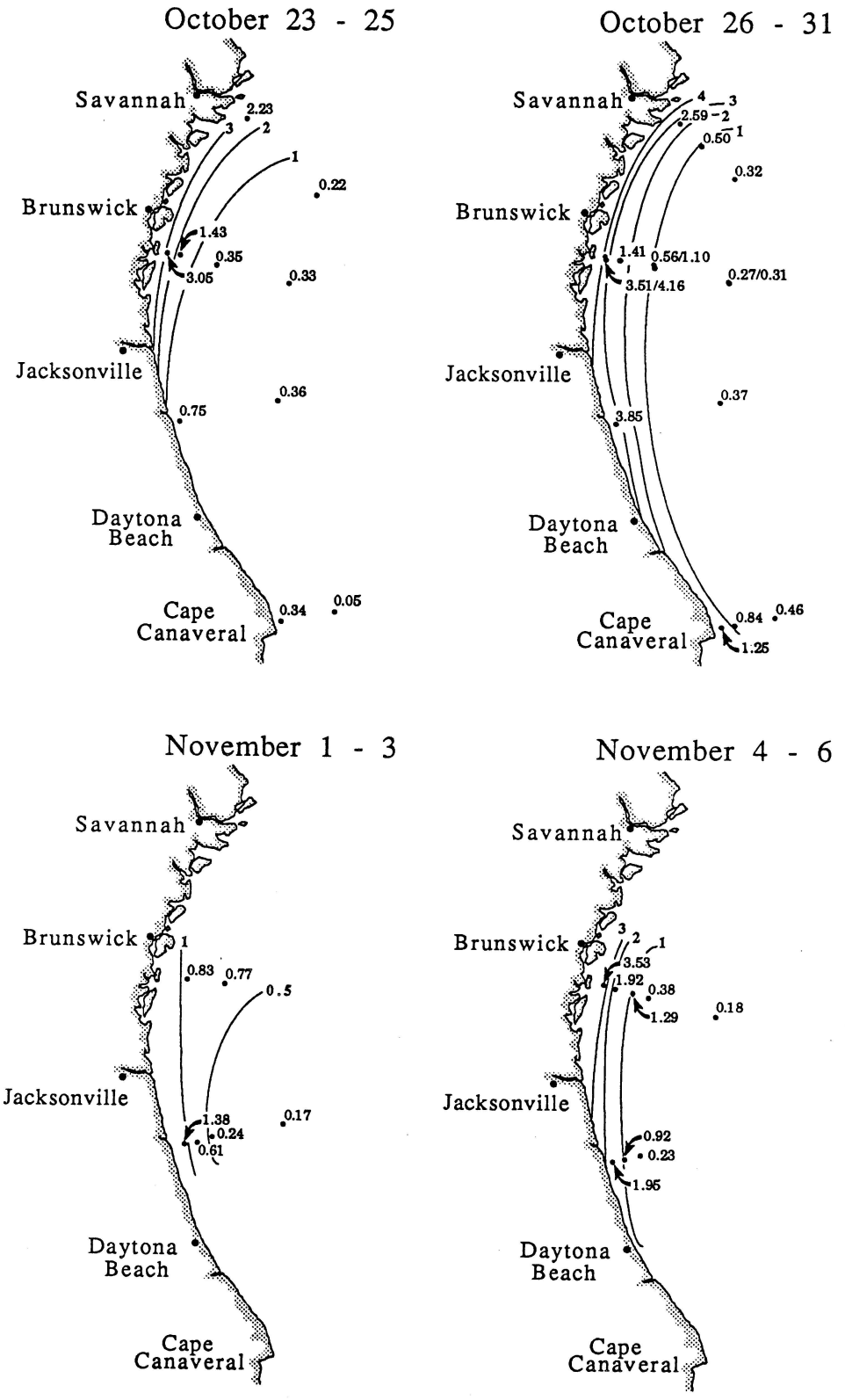

Figure 1. Lignin phenol concentrations ($\mu g\ L^{-1}$) in continental shelf waters of the southeastern U.S. during October and November 1988. Stations with two values (October 26-29 map) were sampled twice, 3 days apart.

One class of soluble compounds produced during the degradation of vascular plant material is lignin-derived dissolved organic matter. As the most refractory component of vascular plant material, lignin-derived DOC appears to be discriminated against as a growth substrate by marine bacteria (Moran and Hodson 1990), allowing measurable quantities to accumulate in the DOC pool. Although it appears that a large fraction of lignin-derived DOC is microbially modified to some extent during or soon after its formation, a portion is identifiable as characteristic lignin phenols (Moran and Hodson 1990). These lignin phenols can be used as tracers of dissolved organic matter originating from degrading vascular plant material, and thus from coastal marshes or inland ecosystems.

In waters off the Georgia coast, concentrations of vanillyl lignin phenols were highest in the nearshore and inner shelf areas, where they ranged from 0.2 to 4.2 $\mu g\ L^{-1}$ (Figure 1). With increasing distance from shore, concentrations gradually decreased, ranging from 0.05 to 0.5 $\mu g\ L^{-1}$ at the shelf edge. Decreases averaged 10-fold across the width of the shelf. There was also evidence of north-south variations in lignin phenol concentrations, particularly for inner shelf samples (Figure 1). Seawater samples collected at the latitudes of Savannah and Brunswick, Georgia, had higher concentrations of lignin-derived material than samples collected further south, at the latitudes of St. Augustine and Cape Canaveral, Florida. Fresh water input is not evenly distributed along the north-south axis of the study area, but instead is concentrated along the Georgia coast (Atkinson and Menzel 1985). Thus the observed longitudinal pattern in lignin phenol concentrations is likely a reflection of the pattern of lignin-rich freshwater discharge from Georgia marshes and rivers.

Lignin phenol concentrations in Georgia continental shelf waters were positively correlated with both DOC and humic carbon content of the seawater samples ($r = 0.72$ and $p < 0.01$ for DOC and $r = 0.94$ and $p < 0.01$ for humic C; Figure 2). Thus greater concentrations of both total DOC and the humic fraction of DOC were found in continental shelf water which also showed evidence of terrestrial (marsh and river) influence. However, lignin phenols did not account for a constant percentage of either the total DOC or dissolved humic carbon pools. Phenols ranged from 0.002 to 0.13% of the bulk DOC, and their quantitative importance decreased seaward, being negatively correlated with salinity ($r = -0.78$ and $p < 0.01$). Likewise, lignin phenols accounted for 0.06 to 0.69% of dissolved humic carbon, with a gradual decrease in importance for more seaward samples ($r = -0.87$ and $p < 0.01$; Figure 3). These data are consistent with there being both terrestrial and oceanic sources of DOC and humic substances (for example, vascular plants, algae, terrestrial and planktonic animal remains, and microbial products), but only terrestrial sources of lignin-derived organic matter. Based on the X-axis intercepts of regression lines on Figure 2, open ocean (essentially lignin-free) water is predicted to have a DOC concentration of 1.1 mg L^{-1} and a humic carbon concentration of 0.09 mg L^{-1} (8% of total DOC). These values are within the ranges previously reported for seawater [1.0 mg L^{-1} DOC for surface (0-300 m) ocean water and 0.06 to 0.60 mg L^{-1} humic C; Thurman 1985].

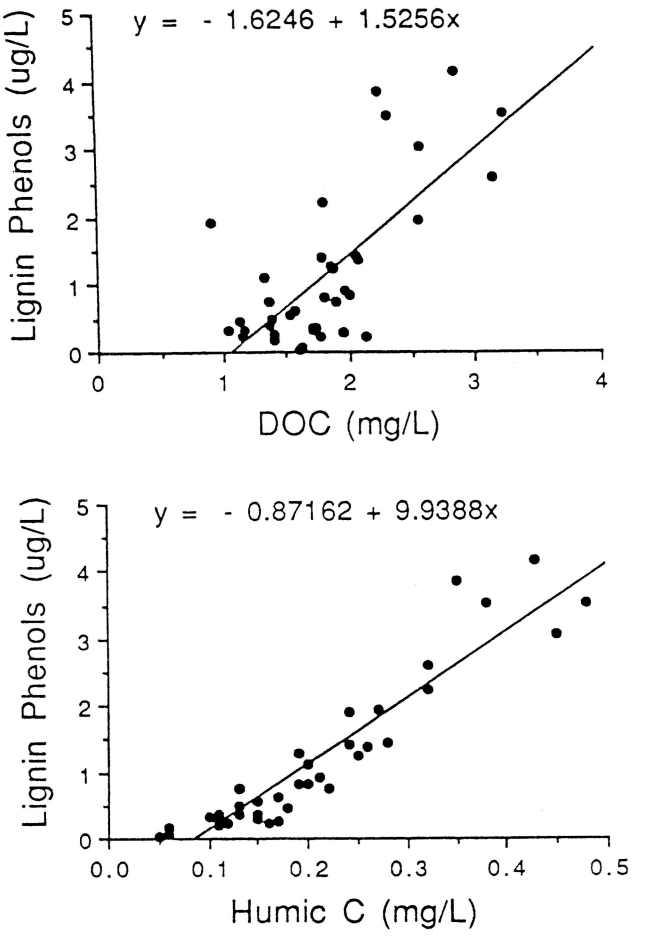

Figure 2. Vanillyl lignin phenol concentrations in Georgia coastal water as a function of total DOC (top) and humic DOC (bottom).

The presence of lignin phenols on the Georgia shelf, and associated high concentrations of total DOC and dissolved humic substances, reinforce the possibility that terrestrially-derived organic matter is important in supporting coastal marine food webs. As a first step toward elucidation of the role of terrestrially-derived DOC, we used lignin phenol concentrations to make a rough estimate of the percent of total continental shelf DOC which is of terrestrial, as opposed to marine, origin. We used a simple mixing model which assumes that lignin-rich waters from coastal marshes and rivers mixes conservatively with lignin-free oceanic water on the shelf (Moran et al., submitted). Based on measures of lignin phenol concentrations in marsh and river samples (0.14 to 1.04 percent of total DOC) compared to concentrations in shelf samples (0.002 to 0.13 percent of total DOC), we roughly estimate that 5 to 36% of the DOC resident on the inner continental shelf off the Georgia coast derives from terrestrial ecosystems, depending on whether the terrestrial DOC source is a river or a marsh, while 3 to 18% of mid to outer shelf DOC is of terrestrial origin (Moran et

al., submitted). The relative availability (quality) of terrestrially-derived DOC vs. marine-derived DOC as a substrate for microbial secondary production in coastal waters is a next important area for research.

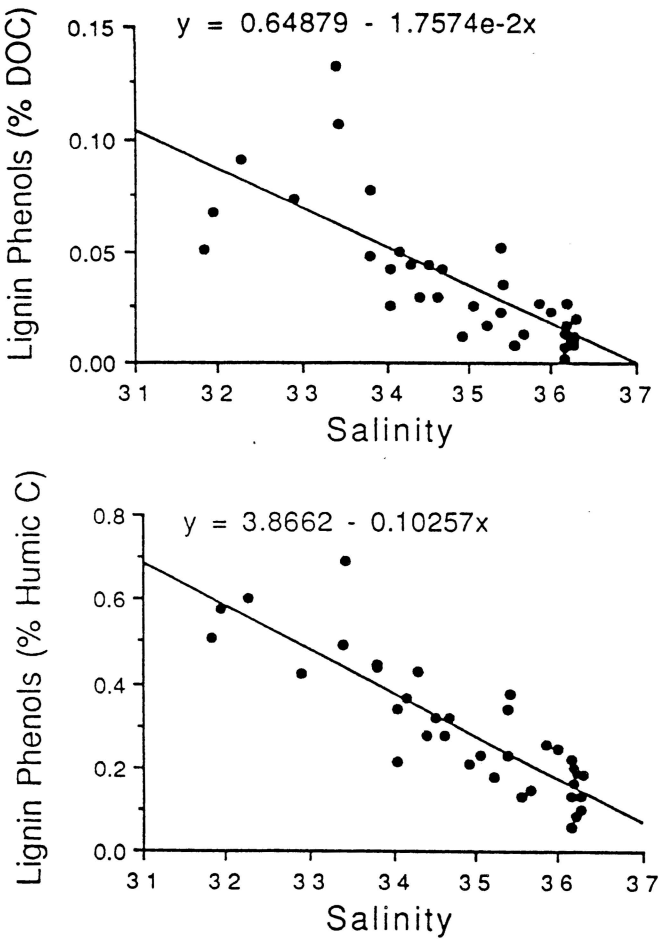

Figure 3. Vanillyl lignin phenols in Georgia coastal waters as a function of salinity. Lignin phenol concentrations are expressed as a percentage of total DOC (top) and humic DOC (bottom).

ACKNOWLEDGMENTS

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